

## NON-CYANIDE SILVER PLATING BATH COMPOSITION

### BACKGROUND OF THE INVENTION

Numerous non-cyanide silver plating processes have been attempted (1). Of these, the only ones to have achieved commercial success have been those employing succinimide, either as a premanufactured silver complex (2, 3), or as a reagent. Succinimide undergoes hydrolysis at pH values above neutrality, which in turn causes the pH of the plating solution, normally in the range of 8 to 9 or so, to become unstable; and also to require frequent replenishment of the succinimide.

Hydantoin (CAS Number 461-72-3) is a cyclic diimide possessing structural features similar to succinimide, and similarly effective as a complexing agent for silver. A series of substituted hydantoins exist, of which the most commonly available commercially is 5,5-dimethylhydantoin (CAS No. 77-71-4). As a class, the hydantoins are soluble in moderate-to-strongly alkaline ( $\text{pH} \geq 8$ ) solutions, are capable of forming complexes with silver and other metals, and are more resistant to hydrolysis than succinimide. Asakawa (4) patented non-cyanide plating solutions for silver in which silver salts are added together with a hydantoin compound and an inorganic or organic acid salt for the purpose of providing electrical conductivity.

Asakawa teaches the use of various sulfur-containing compounds as gloss-controlling agents for the deposits from the plating solutions of his invention, and states that with the use of such additives deposit appearance suitable for decorative applications can be obtained. There is no mention of mirror-bright appearance, however, and the Examples provided do not appear to indicate that mirror-bright deposits would be obtained. In particular, all of the Examples cited include significant quantities of chloride ion, which is a known precipitant for silver and highly likely to form insulating films at the anodes.

Since much commercial silver plating is for the purpose of obtaining mirror-bright to brilliant deposits, it would clearly be desirable to electroplate such deposits from a non-cyanide plating solution, thus saving the costs of cyanide waste treatment, and also of subsequent polishing and buffing.

## SUMMARY OF THE INVENTION

Accordingly, it is an object of this invention to provide a non-cyanide plating solution for the deposition of silver, said solution being capable of yielding mirror-bright to brilliant deposits. It is a further object that the plating solution thus provided be as chemically stable as possible, and free of chemical precipitants.

One preferred embodiment of the present invention is an electroplating solution for the deposition of silver; said solution comprising silver in the form of a complex of silver with hydantoin or a substituted hydantoin compound; said solution also comprising an excess (i.e., more than a stoichiometric amount based on the silver) of the hydantoin or substituted hydantoin compound, together with an effective quantity of a nonprecipitating electrolyte salt, and also an effective quantity of 2,2' dipyridyl for the purpose of obtaining a mirror-bright to brilliant deposit. An excess amount of the hydantoin or substituted hydantoin compound ensures the complete (or nearly complete) complexation of the silver.

Preferably, the electroplating solution further comprises an effective quantity of a pyridine or substituted pyridine compound for the purpose of improving the overall brightness of the deposit obtained. Advantageously, the electroplating solution further comprises an effective quantity of surface-active material for the purpose of further improving the overall brightness and brilliance of the deposit obtained.

In certain preferred embodiments the surface-active material is selected from the group consisting of Hamposyl C, Hamposyl L, Hamposyl O, Blancol, Blancol N, Rhodacal, and Rhodacal N. In certain preferred embodiments, the pyridine or substituted pyridine compound is selected from the group consisting of nicotinamide, isonicotinamide, 2-aminopyridine, 3-aminopyridine, nicotinic acid and its salts, and isonicotinic acid and its salts. In certain preferred embodiments, the nonprecipitating electrolyte salt is selected from the group consisting of the salts of sulfamic, hydrofluoric, nitric, fluoboric, glycolic, and lactic acids.

Another preferred embodiment of the present invention is a process for the formation of a mirror-bright to brilliant electrodeposit of silver on a substrate comprising the step of:

electroplating said substrate in an electroplating solution,  
said solution comprising silver in the form of a complex of silver with hydantoin or a substituted hydantoin compound;  
said solution also comprising an excess of the hydantoin or substituted hydantoin compound, together with an effective quantity of a nonprecipitating electrolyte salt, and an effective quantity of 2,2' dipyridyl for the formation of a mirror-bright to brilliant deposit.

Preferably, the electroplating solution used in the process of the invention further comprises an effective quantity of a pyridine or substituted pyridine compound for the purpose of improving the overall brightness of the deposit obtained. Advantageously, the electroplating solution used in the process of the invention further comprises an

effective quantity of surface-active material for the purpose of further improving the overall brightness and brilliance of the deposit obtained. In certain preferred embodiments the surface-active material is selected from the group consisting of Hamposyl C, Hamposyl L, Hamposyl O, Blancol, Blancol N, Rhodacal, and Rhodacal N. In certain preferred embodiments, the pyridine or substituted pyridine compound is selected from the group consisting of nicotinamide, isonicotinamide, 2-aminopyridine, 3-aminopyridine, nicotinic acid and its salts, and isonicotinic acid and its salts. In certain preferred embodiments, the nonprecipitating electrolyte salt is selected from the group consisting of the salts of sulfamic, hydrofluoric, nitric, fluoboric, glycolic, and lactic acids.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

It has been found that in moderately alkaline ( $\text{pH} \geq 9$ ) plating solutions containing silver in the form of a complex formed with hydantoin or a substituted hydantoin, together with a nonprecipitating electrolyte salt, addition of 2,2'-dipyridyl (CAS No. 366-18-7), either alone or in conjunction with other substituted pyridines and/or surfactants, produces mirror-bright to brilliant deposits.

As used herein, the terms "nonprecipitating electrolyte salts" refer to salts of acids the silver salts of which are soluble. Examples of such nonprecipitating electrolyte salts would include the sodium, potassium, or ammonium salts of sulfamic, hydrofluoric, nitric, fluoboric, glycolic and lactic acids. Such materials do not cause film formation at the anodes, and in some cases promote anode corrosion. Additionally, the silver-hydantoin complexes of this invention are premanufactured in that form to the plating solution, together with an excess of the hydantoin and the nonprecipitating electrolyte salt.

Addition of 2,2'-dipyridyl to the plating solutions of this invention, usually in amounts in the range of about 0.1 to 10 grams per liter, produces bright deposits over a

current density range from about 5-20 mA/cm<sup>2</sup> for solutions operated at room temperature. Addition of further quantities of various substituted pyridine compounds, usually in amounts greater than that of the 2,2'-dipyridyl itself, expands the range of usable current density from about 1 to 30 mA/cm<sup>2</sup>, and improves the uniformity and whiteness of the entire deposit. Preferred substituted pyridine compounds for the purposes of this invention include nicotinamide, isonicotinamide, 2-aminopyridine, 3-aminopyridine, nicotinic acid and its salts, and isonicotinic acid and its salts. These are added in amounts from about 2.5 to 100 grams per liter, depending on other parameters of the plating solution. It should be pointed out that in the absence of 2,2'-dipyridyl, addition of substituted pyridine compounds is generally ineffective for the purposes of this invention. It should also be pointed out that additions of 4,4'-dipyridyl and 1,10-phenanthroline are likewise ineffective for the purposes of this invention.

Finally, it has been discovered that the addition of a suitable surfactant to the plating solutions of this invention containing both 2,2'-dipyridyl and a substituted pyridine compound, produces an overall improvement of deposit brightness from mirror-bright to brilliant. Surfactants suitable for the purposes of this invention include the class of substituted glycine derivatives known commercially as Hamposyls, and also the sulfonated naphthalene - formaldehyde condensate known commercially as Blancol N or Rhodacal N and their aqueous solutions. Both of these classes of surfactants have been used previously for conventional (cyanide based) silver plating.

The plating solutions of this invention produce mirror-bright to brilliant deposits over a range of pH from about 9 to about 13. Certain practical considerations act to limit this range somewhat. The corrosivity of the solutions toward silver anodes increases generally with increasing pH from about pH 9.5 to about pH 13. It also happens that 2,2'-dipyridyl is subject to hydrolysis at pH values above about 10.5, the rate of hydrolysis increasing with increasing pH. In order to obtain adequate replenishment of silver from the anodes and to preserve the useful life of the brightener chemicals, an optimum pH range of about 10-11 is arrived at.

Some Examples of plating solutions of this invention are given as follows. In each of the Examples, silver is added as a preformed complex formed by the reaction of silver oxide with hydantoin, or with a substituted hydantoin, such as 5,5-dimethyl-hydantoin, as appropriate. No foreign ions are thus introduced. Other substituted hydantoin compounds can likewise be employed. Methyl-hydantoin, other alkyl-hydantoins, other dialkyl-hydantoins, and the like are useful herein. See the hydantoin compounds of U.S. Patent No. 5,750,018 for additional examples. This patent is hereby incorporated herein by reference.

#### Example 1

Sufficient water was used to form one liter of a solution containing the following:

Potassium hydroxide	60 grams
Sulfamic Acid	52.5 grams
5,5-dimethylhydantoin	60 grams
Silver as complex with	
5,5-dimethylhydantoin	25 grams Ag
2,2'-dipyridyl	0.8 grams

The solution pH was approximately 11.0. A test panel was plated from this solution in a Hull cell at 0.5 ampere for 5 minutes at room temperature with moving-vane agitation. The deposit obtained was white and mirror-bright at indicated current densities from about 5-20 mA/cm<sup>2</sup>.

#### Example 2

Sufficient water was used to form one liter of a solution containing the following:

Potassium hydroxide	60 grams
---------------------	----------

Sulfamic Acid	52.5 grams
5,5-dimethylhydantoin	60 grams
Silver as complex with	
5,5-dimethylhydantoin	25 grams Ag
2,2 '-dipyridyl	0.40 grams
Nicotinamide	4.0 grams

The solution pH was approximately 11.0. A test panel was plated from this solution in a Hull cell at 0.5 ampere for 5 minutes at room temperature with moving-vane agitation. The deposit obtained was white and mirror-bright at indicated current densities from near zero to about 12.5 mA/cm<sup>2</sup>.

#### Example 3

A plating solution was made up as in Example 2, but additionally containing approximately 0.6 grams of Rhodacal N in the form of an aqueous solution. A test panel was plated from this solution in a Hull cell at 0.5 ampere for 5 minutes at room temperature with moving-vane agitation. The deposit obtained was brilliant mirror-bright white at current densities from near zero to greater than 20 mA/cm<sup>2</sup>.

#### Example 4

A plating solution was made up as in Example 3 except containing approximately 0.4 grams of Hamposyl L as an aqueous solution solubilized by potassium hydroxide in place of the Rhodacal N. A test panel was plated from this solution in a Hull cell at 0.5 ampere for 5 minutes at room temperature with moving-vane agitation. The deposit obtained was brilliant mirror-bright white at current densities from near zero to greater than 20 mA/cm<sup>2</sup>.

#### Example 5

A plating solution was made up as in Example 3 except containing 1.3 grams of 2-aminopyridine in place of nicotinamide. A test panel was plated from this solution in a Hull cell at 0.5 ampere for 5 minutes at room temperature with moving-vane agitation. The deposit obtained was brilliant mirror-bright white at current densities from near zero to greater than 20 mA/cm<sup>2</sup>.

#### Example 6

A plating solution was made up as in Example 5 except containing 0.8 grams of 3-aminopyridine in place of 2-aminopyridine. A test panel was plated from this solution in a Hull cell at 0.5 ampere for 5 minutes at room temperature with moving-vane agitation. The deposit obtained was brilliant mirror-bright white at current densities from near zero to greater than 20 mA/cm<sup>2</sup>.

#### Example 7

Sufficient water was used to form one liter of a solution containing the following:

Potassium hydroxide	45 grams
Sulfamic Acid	45 grains
Hydantoin	45 grams
Silver as complex	
with hydantoin	25 grams Ag
2,2' dipyridyl	2.64 grams

The solution pH was approximately 11.0. A test panel was plated from this solution in a Hull cell at 0.5 ampere for 5 minutes at room temperature, with moving-



vane agitation. The deposit obtained was white and hazy-bright from near zero to about 5 mA/cm<sup>2</sup>.

#### Example 8

A plating solution was made up as in Example 7 except additionally containing 26.4 grams of nicotinamide. A test panel was plated from this solution in a Hull cell at 0.5 ampere for 5 minutes at room temperature with moving-vane agitation. The deposit obtained was white and mirror-bright at current densities from near zero to greater than 20 mA/cm<sup>2</sup>.

#### Example 9

A plating solution was made up as in Example 8 except additionally containing 0.16 grams of Hamposyl L in the form of an aqueous solution solubilized with potassium hydroxide. A test panel was plated from this solution in a Hull cell at 0.5 ampere for 5 minutes at room temperature with moving-vane agitation. The deposit obtained was brilliant mirror-bright white at current densities from near zero to 20 mA/cm<sup>2</sup>.

It will be apparent to those skilled in the art that the Examples provided herein are illustrative of the present invention, but do not represent the totality of the useful embodiments thereof.

The following documents, cited above, are hereby incorporated herein by reference:

1. Modern Electroplating, 4<sup>th</sup> Edition, M. Schelesinger and M. Paunovic, Eds., John Wiley, New York 2000, pp. 227 ff.
2. E. Hradil, H. Hradil, and A. M. Weisberg, U.S. Patent 4,126,524 (1978).
3. E. Hradil, H. Hradil and A. M. Weisberg U. S. Patent 4,246,077 (1981).
4. T. Asakawa, U. S. Patent 5,601,696 (1997)

5. W. Brasch, U. S. Patent 5,750,018 (1998)